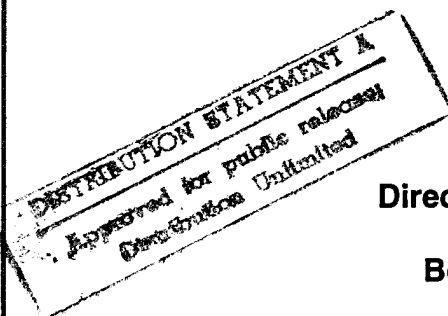# High Temperature Reaction Kinetics of Boron Oxides

Final Report
for June 15, 1991 through September 30, 1994

CONTRACT NO. F49620-91-C-0057
PROJECT NO. 2308/A2
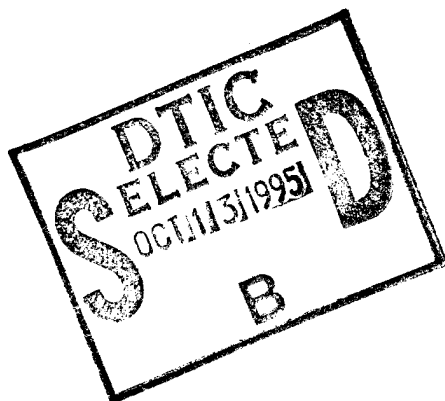
Prepared for:

AFOSR/NA
Directorate of Aerospace Sciences
Building 410
Bolling AFB, DC 20332-6448
Attn: Dr. Julian Tishkoff

Prepared by:

Allen Twarowski
Principal Investigator

DTIC
SELECTED
OCT 13 1995
B

AUGUST 1994

19951011 152

DTIC QUALITY INSPECTED 5

Rockwell International
Science Center

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE **August 1994**	3. REPORT TYPE AND DATES COVERED **Final Technical Report (06/15/91—09/30/94)**

4. TITLE AND SUBTITLE

High Temperature Reaction Kinetics of Boron Oxides

5. FUNDING NUMBERS

PE - 61102F
PR -2308
SA - BS
F49620-91-C-0057

4. AUTHOR(S)

A.J. Twarowski

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

**Rockwell Science Center
1049 Camino Dos Rios
Thousand Oaks, CA 91360**

7. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

**AFOSR/NA
110 Duncan Avenue, Suite B115
Bolling AFB, DC 20332-0001**

9. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTING/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

Kinetics experiments performed under this contract show a much larger rate of H+OH recombination at high temperature (1500–2500 K) when phosphine combustion products are present in the gas mixture. A kinetic mechanism has been developed for phosphorus species participation in the reaction chemistry. This mechanism has been used to fit both OH decay signals and H_2O hot band absorbance signals in H_2O laser photolysis experiments. The temperature dependence of the phosphorus reaction system was measured with laser photolysis experiments and a sensitivity analysis selected the key chemical reactions that drive H+OH recombination (and H+H recombination) in phosphorus species-containing gases. Rate constants for phosphorus bimolecular reactions were estimated using standard kinetics assumptions. Rate constants for recombination reactions were estimated using a simplified version of RRKM theory. Agreement between OH decay measurements in photolysis experiments and computed OH time profiles using the phosphorus mechanism developed in this contract is reasonably good.

Computer simulations of SCRAM-jet nozzle gas flow using 1-D hydrodynamics coupled with the phosphorus kinetic mechanism show a large increase in heat release *per unit fuel mass* in the nozzle when phosphine is included in hydrogen fuel. These same computer calculations predict a net increase in fuel specific impulse under fuel rich conditions. Optimization of nozzle design for hydrogen fuel with a phosphine additive may realize even more gain in specific impulse.

14. SUBJECT TERMS
Reaction rates, phosphine, phosphorous oxide, recombination, kinetics, photolysis, thermochemical rate constant.

15. NUMBER OF PAGES
14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT **UNCLASSIFIED**	18. SECURITY CLASSIFICATION OF THIS PAGE **UNCLASSIFIED**	19. SECURITY CLASSIFICATION OF ABSTRACT **UNCLASSIFIED**	20. LIMITATION OF ABSTRACT **UL**

Rockwell

Science Center

SC71053.FR

Table of Contents

List of Figures

Figure   **Page**

Summary of Research Progress

Objective

Catalysis of heat-releasing H+OH recombination in the nozzle section of a SCRAM-jet potentially increases the fuel efficiency and therefore the thrust of a hydrogen-fueled, air-breathing, hypersonic aircraft. Phosphine (PH_3) combustion products substantially increase the rate of disappearance of excess OH when present in a mixture of partially photolyzed water vapor. The objectives of this research program were to 1) determine the identity and equilibrium densities of phosphorus combustion products present in the gas phase when phosphine is burned with oxygen, 2) construct a reaction model including the most abundant phosphorus species, 3) determine the rate constants for reactions of phosphorus combustion products in a high temperature gas, and 4) identify the mechanism by which phosphorus combustion products increase the disappearance rate of excess OH density in a water photolysis experiment. To assess the potential effectiveness of H+OH $\rightarrow$ H_2O catalysis, the reaction mechanism developed in this study was used in a computer model of SCRAM-jet reaction kinetics to predict the gain in heat release in the nozzle from phosphorus combustion products and to calculate the increase in specific impulse resulting from the heat release gain.

Results

Photolysis Experiments

Hydrogen reacts with oxygen at high temperature to produce water vapor and a considerable amount of heat. In our combustion reactor, gas temperatures of 1500–2500 K are achieved at pressures of 300–700 Torr. At these temperatures the equilibrated combustion products consist of small but significant amounts of radicals such as OH and H. To probe the reaction chemistry of the combustion products, the equilibrated system is perturbed by laser photolysis of H_2O, which substantially increases the pool of OH and H radicals.

In one set of experiments [1], the return of the system to equilibrium is experimentally investigated by recording, as a function of time, the OH absorption of a frequency-doubled cw-dye laser probe beam producing 312 nm radiation. The OH absorption signal is recorded on a digital oscilloscope and transferred as a binary file to a computer for subsequent analysis.

Figure 1 shows the dramatic effect on the rate of recovery of the OH signal when PH_3 is added to the hydrogen fuel and burned with oxygen. Photolysis occurs at 0.1 ms on the graph and results in a very fast increase in OH absorbance (the value plotted in Fig. 1 is the *change* in OH absorbance from the equilibrium level). When phosphine is not present in the hydrogen fuel stream, the OH signal relaxes back towards its equilibrium value at a slow rate represented by the empty squares plotted in Fig. 1. The rate at which OH absorbance returns to its equilibrium value is increased dramatically by the addition of 0.1% by volume phosphine in the hydrogen flow stream (filled circles). The addition of phosphine in amounts as small as 0.03% by volume (not shown in this figure) results in a significant increase in OH disappearance rate.
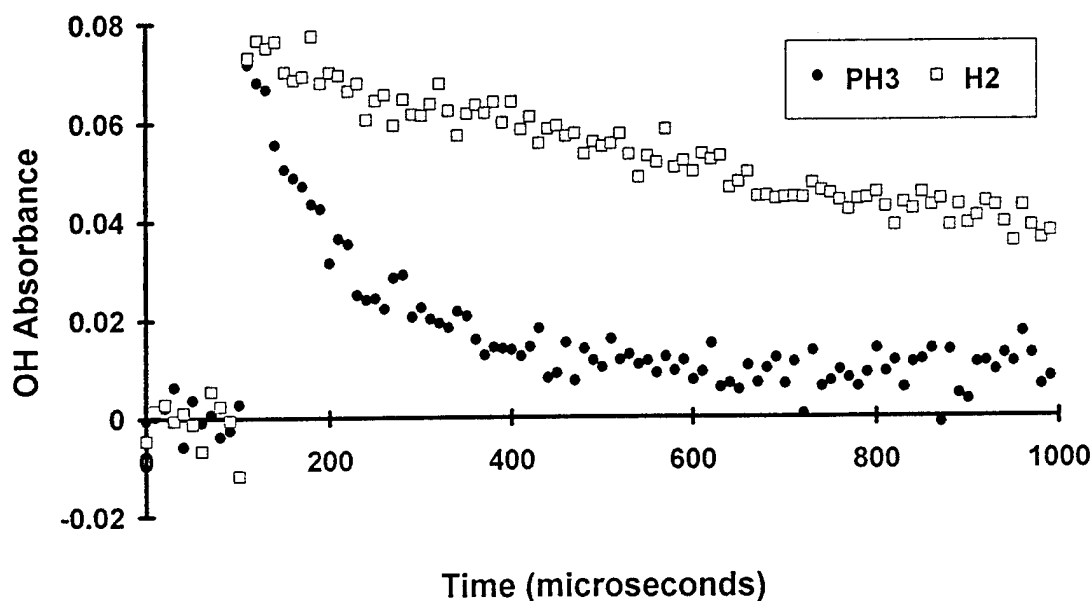

Time (microseconds)

Fig. 1   OH density change following H_2O photolysis. Test gas mixture is the combustion products of H_2(empty squares) and 0.1% PH_3/H_2 (filled circles). Rich fuel mixture.

The more rapid disappearance of excess OH when PH_3 combustion products are present in the photolyzed test gas is not proof of an increased rate of H+OH recombination. One may argue that a fast bimolecular reaction step consumes OH but does not generate H_2O until much later. To more completely test the hypothesis that PH_3 combustion products catalyze the overall rate of H+OH recombination, the product side of this reaction was measured [2]. An H_2O absorbance signal at 192 nm resulted from a rise in temperature caused by heat released when the photolysis products, H and OH, recombine.

Figure 2 shows a typical H_2O absorbance signal for a fuel-rich test gas mixture. The absorbance change shown in the figure was calculated by taking the decadic logarithm of the

average signal (time series of photodetector output) recorded prior to the photolysis pulse divided by the signal itself. The signal slowly increases to a positive limiting value of about 0.003 after photolysis. The shape of the signal suggests the appearance of a product developing over the 0.9 ms experimental time period. For this experiment, photolysis of H_2O by the excimer laser creates excess OH and H radical. When the radicals eventually recombine the laser energy used in photolyzing H_2O appears as thermal energy which raises the temperature of the gas. The signal at 192 nm is in a spectral region where the absorbance of H_2O increases with temperature. Therefore, the transient absorbance signal at 192 nm has two components that are superposed, an initial decrease in the absorbance signal due to a decrease in H_2O density and a gradual increase in the absorbance signal due to a change in the absorption coefficient caused by an increase in temperature. Calculations show that the signal expected at 192 nm is predominately determined by the temperature-driven increase in the absorption coefficient of H_2O when recombination reactions release the photolysis energy stored in the population of excess OH and H radicals.
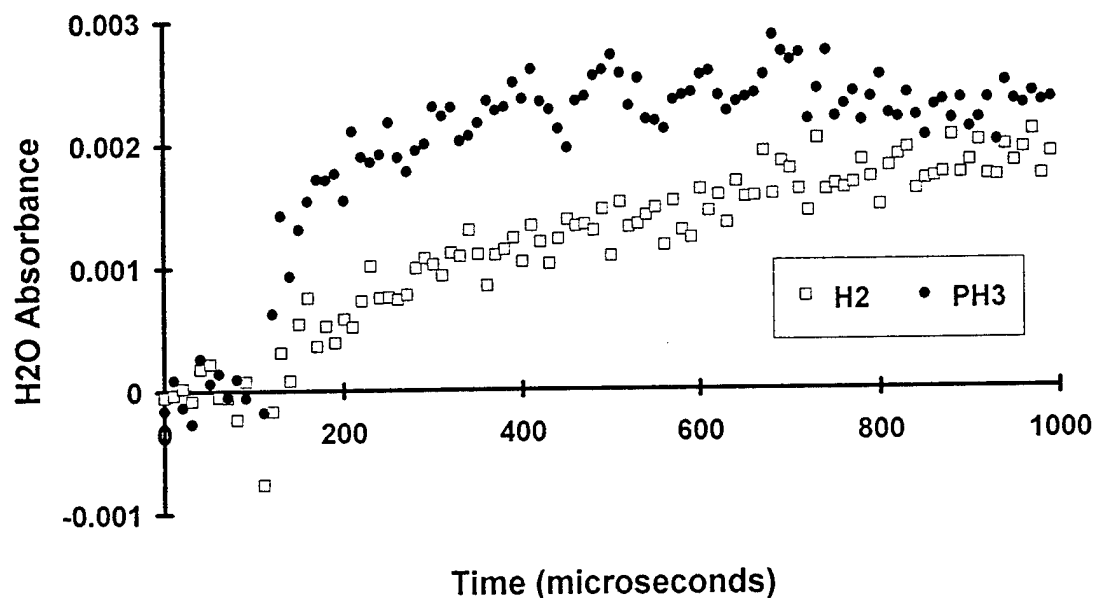

Fig. 2 H_2O absorbance change following H_2O photolysis. Test gas mixture is the combustion products of H_2(empty squares) and 0.1% PH_3/H_2(filled circles). Rich fuel mixture.

As Fig. 1 shows, phosphine combustion products, when present at relatively low density, substantially increase the rate at which the OH density returns to its equilibrium value following H_2O photolysis. If the more rapid relaxation rate for the OH signal is the result of an increased net H+OH recombination rate, then the H_2O signal should rise more quickly to its limiting value when PH_3 combustion products are present in the test gas mixture. Figure 2 compares the H_2O

absorbance signals recorded with and without 0.1% PH_3 present in the H_2 fuel stream for a fuel rich combustion mixture. A faster rise in the H_2O signal at earlier times is observed when PH_3 is added to the fuel indicating a faster release of heat caused by more rapid H+OH recombination.

The observed H_2O signals are consistent with the OH measurements and model calculations.

Reaction Model

A kinetic model was constructed to analyze the experimental OH and H_2O absorbance signals and the effect of phosphine combustion products on these signals. A list of those phosphorus species (PO, PO_2, PO_3, HOPO, $HOPO_2$, HPO, P_2O_3, H_2POH, HPOH, P_2O_2, P_2O, PH_3, PH_2, PH, P_4, P_2, P) that potentially participate in the reaction chemistry was assembled, and the thermodynamic properties of each species was either taken from literature reports or estimated from quantum chemical calculations reported in the literature [1].

In the original reaction model proposed [1], the equilibrium densities of the 17 phosphorus species were calculated under conditions of the photolysis experiment. Species that did not have a large enough density to cause an increase in the H+OH recombination rate even at collision-controlled rates were eliminated from further consideration. A reaction model was constructed from reactions of the remaining species.

In subsequent work [3], a computer program was written to list all possible bimolecular and recombination reactions occurring among the 17 phosphorus species. Another program estimated the rate constants for the bimolecular reactions; rate constants for the recombination reactions were estimated using a simplified RRKM calculation [1]. A reaction model reduction analysis was used to select those reactions that contribute to the overall rate of H+OH recombination in a gas that has been initially removed from chemical equilibrium by H_2O photolysis or by a temperature jump perturbation. A thermodynamic free energy function was used to quantify the rate of system relaxation back to equilibrium for a series of 36 reaction conditions covering a temperature range of 1500 to 3000 K, a gas density range of 5×10^{-7} to 5×10^{-5} moles/cm^3 and a fuel equivalence ratio of 0.8 to 1.2. The reactions that show the greatest participation in equilibrium relaxation kinetics by this analysis are listed below in Table 1. Criterion for inclusion of a reaction in the table is that the reaction have an analysis factor (defined in reference 3) larger than 0.0001 under any set of gas conditions for either temperature or photolysis perturbation.

Table 1. Selected Reactions and Associated Analysis Factors

Reaction	Analysis Factor	
	Temp	Photo
H + PO2 = HOPO	0.7958	0.6878
H + HOPO = H2 + PO2	0.5104	0.5136
OH + PO2 = HOPO2	0.4139	0.2911
PO + PO2 = P2O3	0.3517	0.0009
O + HOPO2 = O2 + HOPO	0.1437	0.0710
O + HOPO = OH + PO2	0.0830	0.0433
OH + HOPO = H2O + PO2	0.0821	0.0054
PO + HOPO2 = PO2 + HOPO	0.0791	0.0002
H + HOPO = H2O + PO	0.0762	0.0106
H + HOPO2 = H2O + PO2	0.0329	0.0170
O + HOPO = HOPO2	0.0233	0.0087
O + PO = PO2	0.0083	0.0038
HO2 + PO2 = OH + PO3	0.0054	0.0005
HO2 + PO2 = O + HOPO2	0.0053	0.0004
O2 + PO = O + PO2	0.0051	0.0045
P2 + P2 = P4	0.0038	0.0000
HO2 + PO2 = O2 + HOPO	0.0038	0.0001
H + PO = HPO	0.0027	0.0028
H + HPO = H2 + PO	0.0021	0.0021
OH + P2O3 = PO2 + HOPO	0.0018	0.0000

Reaction	Analysis Factor	
	Temp	Photo
OH + PO = H + PO2	0.0017	0.0009
PO2 + P = PO + PO	0.0015	0.0013
O + PO3 = O2 + PO2	0.0013	0.0009
H2O + PO3 = OH + HOPO2	0.0009	0.0027
O + PO2 = PO3	0.0006	0.0083
OH + PO = HOPO	0.0005	0.0001
OH + P = H + PO	0.0004	0.0004
H + P2O3 = PO + HOPO	0.0003	0.0097
OH + HOPO = H + HOPO2	0.0003	0.0008
O2 + P = O + PO	0.0003	0.0003
O + HPO = OH + PO	0.0002	0.0002
H + PO3 = OH + PO2	0.0002	0.0013
HOPO2 + P = PO + HOPO	0.0002	0.0000
H + HPO = HPOH	0.0001	0.0002
PO + HPOH = HOPO + PH	0.0001	0.0000
O + P2O3 = PO2 + PO2	0.0001	0.0003
H + PO3 = O + HOPO	0.0001	0.0010
O + P2O3 = PO + PO3	0.0000	0.0027
O + P2 = PO + P	0.0000	0.0001

Most of the reactions originally selected for inclusion in a reaction model (in reference 1) are present in Table 1. Conclusions reached concerning catalysis reaction schemes that are of importance for H+OH recombination are unchanged by the more rigorous analysis. The most likely reaction sequence catalyzing both H+H and H+OH recombination is

$$H + PO_2 \rightarrow HOPO$$
$$H + HOPO \rightarrow H_2 + PO_2$$
$$OH + H_2 \rightarrow H_2O + H \qquad .$$
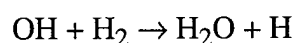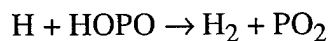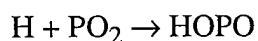
Temperature Dependence of Rate Constants [5]

The relaxation rate of OH density back to equilibrium following H_2O photolysis was recorded under fuel rich conditions at gas temperatures in the range of 1500–2500 K. A reaction model consisting of a standard set of 13 H_2/O_2 reactions and seven of the most important (as determined by the reaction model reduction analysis) phosphorus reactions was used to fit the OH decay signals.

The laser photolysis experiments consisted of two sets of data; those in which about 0.1% phosphine in hydrogen was burned with oxygen and those in which phosphine was not included.

The pure H_2 data set was analyzed by allowing the rate constants for all 13 reactions to vary. After the optimal set of rate constants was calculated (those that minimized the deviation of computed from experimental OH absorbance signal), each rate constant was allowed to vary separately and a range of values for each rate constant was calculated over which the deviation did not change by more than 10%. Most of the rate constants had a very wide range of values indicating the relative insensitivity of the computed OH signal to the value of the rate constant. However, the deviation of computed from experimental OH absorbance signal showed the expected relatively high sensitivity to the value of the rate constant for the $H + OH + M \rightarrow H_2O + M$ reaction. The rate constant for this recombination reaction displayed a temperature dependence that differed substantially from that of the accepted literature value. Figure 3 shows a graph of $Log_{10}[k/k_0]$ versus temperature for the H+OH recombination reaction, where k is rate constant derived from the analysis and $k_0 = 8.32 \times 10^{21}T^{-2}$.

The PH_3/H_2 data was analyzed in a manner similar to that of the pure H_2 data. However, for this data set only the seven rate constants associated with the seven phosphorus-containing reactions were used as parameters in the fit (the H_2/O_2 rate constants were fixed at their standard values). The result of this analysis showed an insensitivity of the computed OH signal to all but the $H + PO_2 \rightarrow HOPO$ and $H + HOPO \rightarrow H_2 + PO_2$ reactions. While both these reactions showed a temperature dependence that deviated at some temperatures from the baseline values, a trend was not evident in the data. In Fig. 4 below, a graph of $Log_{10}[k/k_0]$ versus temperature for the $H + PO_2 \rightarrow HOPO$ reaction is shown.

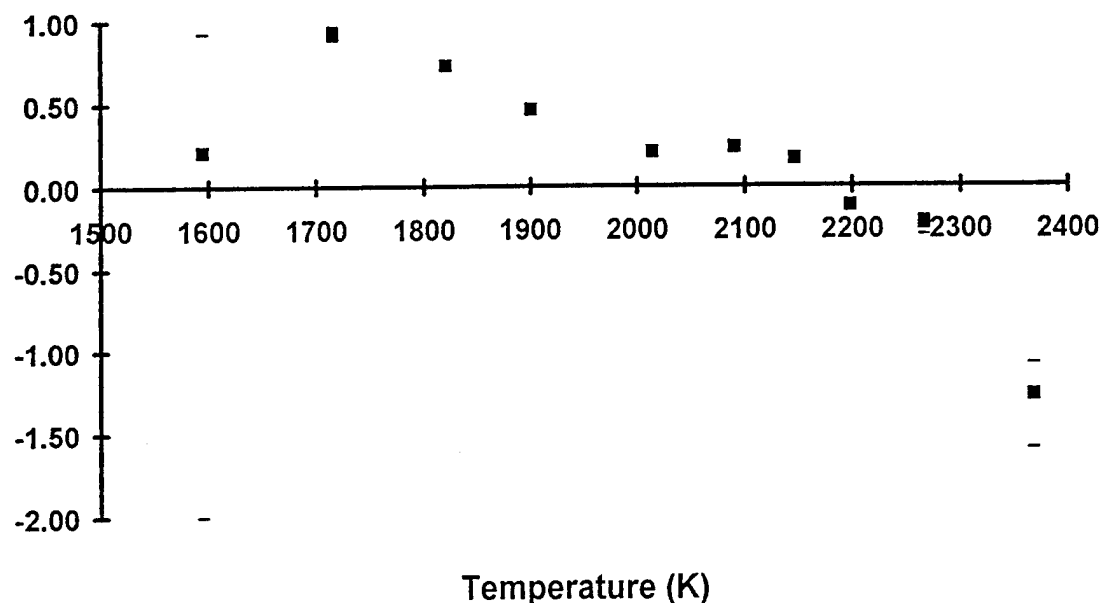Fig. 3 $Log_{10}[k/k_0]$ versus temperature where k is the rate constant calculated for the H + OH + M $\rightarrow H_2O$ + M reaction and $k_0 = 8.32 \times 10^{21}T^{-2}$.

Temperature (K)
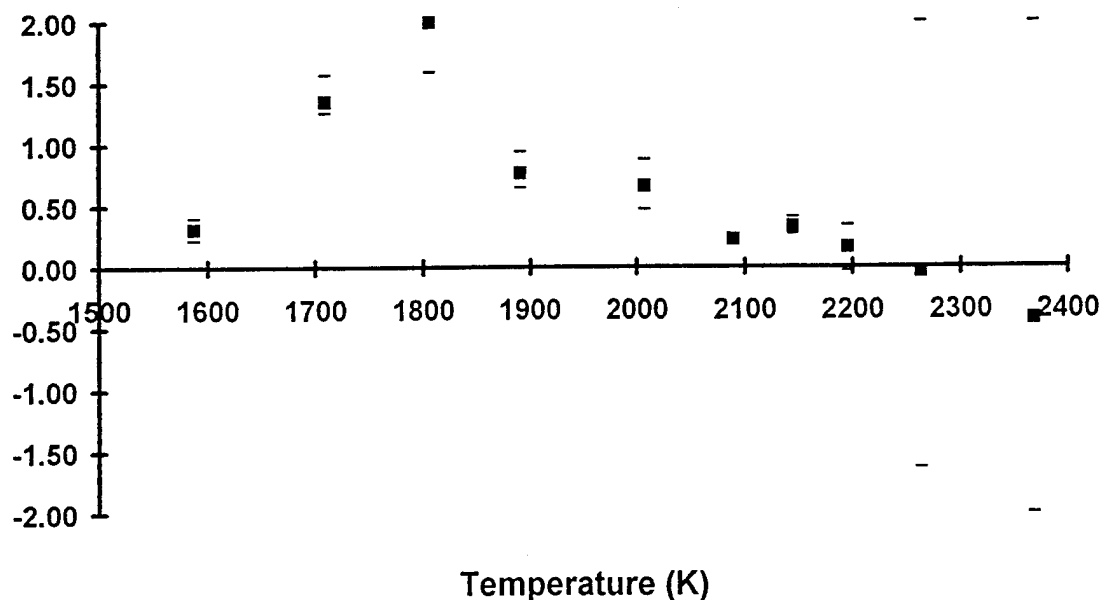

Fig. 4 $Log_{10}[k/k_0]$ versus temperature where k is the rate constant calculated for the H + PO$_2$ $\rightarrow$ HOPO reaction and k_0 is the baseline value of this rate constant.

Temperature (K)

Nozzle Performance Calculations [4]

It is generally believed that hypersonic aircraft will suffer from diminished fuel efficiency as a consequence of slow radical recombination in the aircraft nozzle. A faster recombination rate may allow increased heat release in the nozzle and increased thrust when the thermal energy is converted to directed gas flow by nozzle expansion. Whether a homogeneous catalyst, such as a mixture of phosphine combustion products, can increase the overall system performance of a hypersonic vehicle will depend on the trade-off between the extra weight of the catalyst and the benefit realized by the additional energy released in the nozzle.

A series of simple one-dimensional nozzle expansion calculations in which the heat released per unit of fuel mass was compared with and without phosphine addition to the fuel were performed. The calculations assumed adiabatic reaction of hydrogen fuel with air. A chemically equilibrated gas of combustion products entered the nozzle section of the SCRAM-jet. The nozzle was assumed to be rectangular in cross section and expand in one dimension only. The heat released per unit fuel mass by the flowing gas in the nozzle was calculated as a function of nozzle length. Comparisons between pure H_2 fuel and H_2 containing PH_3 revealed that the latter released additional heat throughout the length of the nozzle for fuel-rich combustion conditions, as shown in Fig. 5.
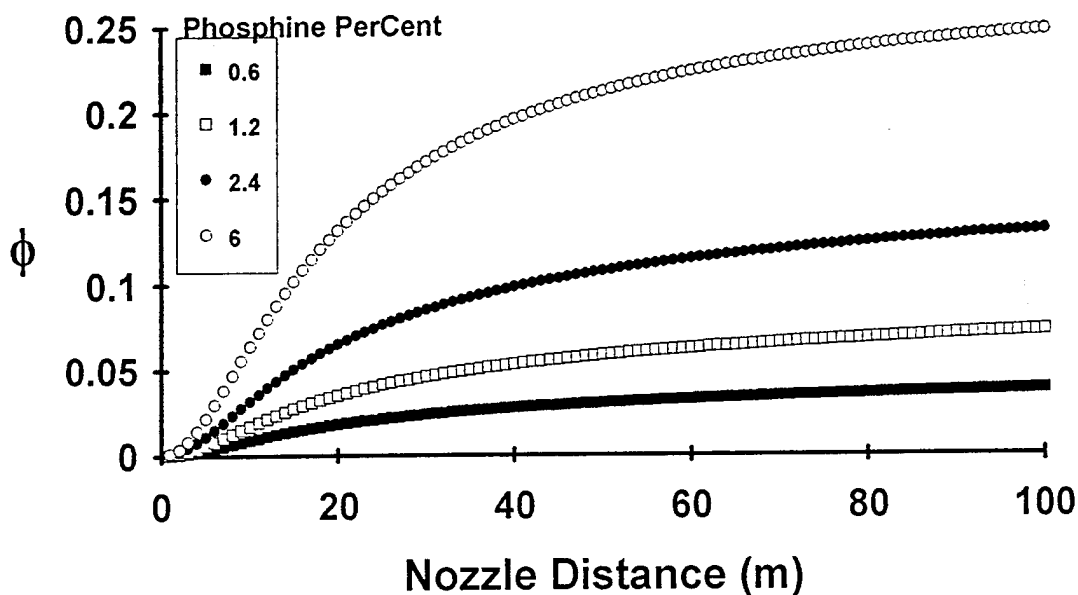

Fig. 5 Fractional increase in heat release, ϕ, versus nozzle distance. Fuel mixture has an equivalence ratio of nominally 1.2, and the gas velocity at the nozzle entrance is 5000 m/s.

The difference in specific impulse of the pure H_2 and H_2/PH_3 fuels was also calculated. In Fig. 6 the specific impulse gain realized by the addition of PH_3 to the fuel is graphed as a function of mass per cent PH_3 in the fuel with the initial gas velocity as a parameter. These calculations were done for a slightly fuel-rich reaction mixture. For this nozzle geometry, the specific impulse gain appears to reach a maximum at 2–3 per cent by mass phosphine in the fuel. While the values of specific impulse gain are not large, no effort was made in this study to optimize the nozzle design for the phosphine fuel additive.
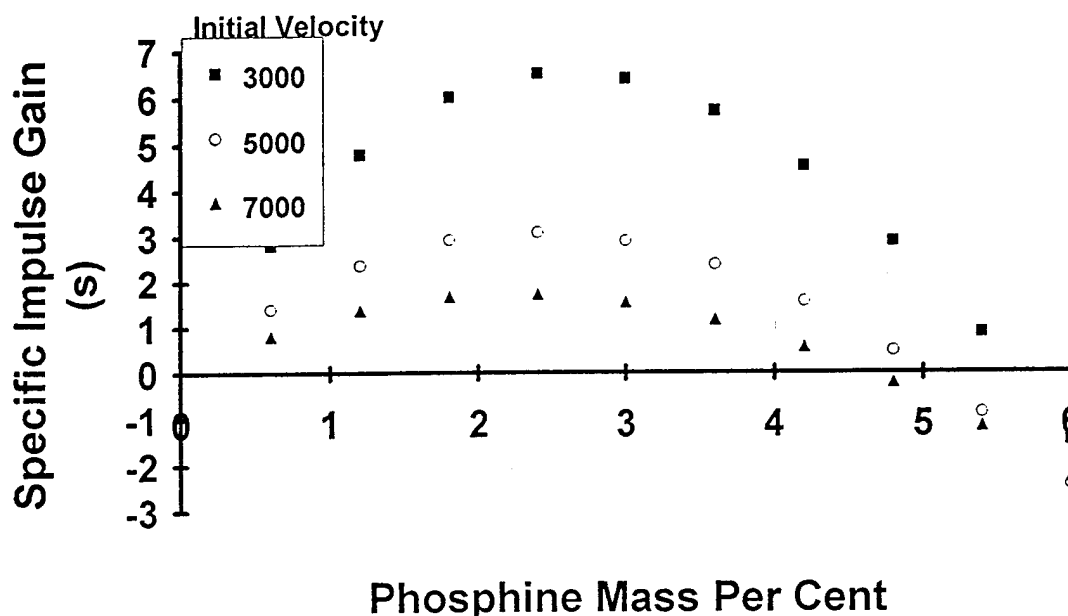

Fig. 6 The gain in specific impulse from phosphine addition. The phosphine mass per cent is indicated on the abscissa.

Personnel

A.J. Twarowski—Principal Investigator

Publications

1. A.J. Twarowski, "The Influence of Phosphorus Oxides and Acids on the Rate of H+OH Recombination", *Combustion and Flame,* **94**: 91–107 (1993).

2. A.J. Twarowski, "Photometric Determination of the Rate of H_2O Formation from H and OH in the Presence of Phosphine Combustion Products", *Combustion and Flame,* **94**: 341–348 (1993).

3. A.J. Twarowski, "Reduction of a Phosphorus Oxide and Acid Reaction Set", *Combustion and Flame,* accepted for publication.

4. A.J. Twarowski, "The Effect of Phosphorus Chemistry On Recombination Losses in a Supersonic Nozzle", *Combustion and Flame,* accepted for publication.

5. A.J. Twarowski, "The Temperature Dependence of H+OH Recombination in Pure H_2 and PH_3/H_2 Post-Flame Gases", manuscript in preparation.